

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2002-060422

(43)Date of publication of application : 26.02.2002

---

(51)Int.Cl. C08F 8/32

---

(21)Application number : 2000-244223 (71)Applicant : YOKOHAMA RUBBER CO  
LTD:THE

(22)Date of filing : 11.08.2000 (72)Inventor : CHINO KEISUKE

---

## (54) THERMOPLASTIC ELASTOMER

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To obtain a thermoplastic elastomer than can exhibit sufficient melt fluidity at a temperature at which a common thermoplastic resin is molded, forms a stable crosslinked structure developing rubber elasticity at ordinary temperature, and can alternate curing and fluidization as its temperature changes, to provide a method for producing the same, and to obtain a rubber composition using the same.

**SOLUTION:** Use is made of a thermoplastic elastomer having as side chains at least two members selected from the group consisting of an aromatic ring having a substituent which a positive substituent constant  $\alpha$  of the Hammett's rule, an aromatic ring having a substituent with a negative  $\alpha$ , an aromatic ring having no substituent with an  $\alpha$  of 0, and a nitrogen-containing heterocyclic ring.

---

## LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of  
rejection]

[Kind of final disposal of application other than  
the examiner's decision of rejection or  
application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's  
decision of rejection]

[Date of requesting appeal against examiner's  
decision of rejection]

[Date of extinction of right]

## CLAIMS

---

### [Claim(s)]

[Claim 1] The ring in which the substituent constant sigma of Hammett's rule has the substituent of a forward value, the ring in which said sigma has the substituent of a negative value, thermoplastic elastomer to which said sigma has at least two sorts chosen from non-permuted the ring and nitrogen-containing heterocycle of 0 in a side chain.

[Claim 2] Thermoplastic elastomer according to claim 1 which has at least two sorts chosen from the ring in which said sigma has the substituent of a forward value, the ring in which said sigma has the substituent of a negative value, and nitrogen-containing heterocycle in a side chain.

[Claim 3] claim 1 whose substituent of a forward value is at least one sort as which said sigma is chosen from a halogen radical, a phenyl group, a cyano group, a nitro group, an acetyl group, and a carboxyl group -- or thermoplastic elastomer given in 2.

[Claim 4] Thermoplastic elastomer according to claim 1 to 3 whose substituent of a negative value is at least one sort as which said sigma is chosen from an alkyl group, a methoxy group, a phenoxy group, a hydroxyl group, and the amino group.

[Claim 5] Thermoplastic elastomer according to claim 1 to 4 which has the ring in which said sigma has the substituent of a forward value, and the ring in which said sigma has the substituent of a negative value in a side chain.

[Claim 6] Thermoplastic elastomer according to claim 1 to 4 which has the ring in which said sigma has the substituent of a forward value, and nitrogen-containing heterocycle in a side chain.

[Claim 7] Thermoplastic elastomer according to claim 1 to 6 which furthermore has a carbonyl content radical in a side chain.

[Claim 8] The rubber constituent containing thermoplastic elastomer according to claim 1 to 7.

---

## DETAILED DESCRIPTION

---

### [Detailed Description of the Invention]

#### [0001]

[Field of the Invention] This invention relates to the thermoplastic elastomer which repeats arch forming and bridge formation dissociation by the temperature change, and can be reproduced, and the manufacture approach and the rubber constituent using it.

#### [0002]

[Description of the Prior Art] To the conventional vulcanized rubber which has the stable three-dimensional network which carried out covalent bond, a high polymer and a vulcanizing agent can use physical bridge formation, and can carry out fabrication of the thermoplastic elastomer easily by heating melting like thermoplastics, without needing complicated vulcanization and forming cycle containing preforming etc. As an example of a type of such thermoplastic elastomer, including the resinous principle and the rubber component, a microcrystal nature resinous principle serves as a hard segment which plays the role of the point of a three-dimensional network constructing a bridge, and prevents the plastic deformation of a rubber component (soft segment), and the thermoplastic elastomer deformed plastically by softening or fusion of a resinous principle is known for

ordinary temperature according to the temperature up. However, in such thermoplastic elastomer, since the resinous principle is included, rubber elasticity tends to fall.

Therefore, the ingredient which can give thermoplasticity, without including a resinous principle is called for.

[0003] On the other hand, reuse of a used ingredient is desired from positions, such as environmental protection and saving resources, in recent years. In such a situation, as for thermoplastics, such as olefin system thermoplastics, the method of performing bridge formation processing by use of a silanol condensation reaction etc. is used abundantly for amelioration, such as a mechanical strength at the time of thermal resistance and an elevated temperature. However, the resin used as the bridge formation object by this approach does not have thermoplasticity any longer, but since the reuse by melting shaping is impossible, coexistence of a bridge formation object and thermoplasticity is called for strongly. This invention persons indicated that the elastomer constituent containing the elastomer which has previously the reactive site which can form hydrogen bond, and the compound which has the reactive site of this elastomer and the reactive site which can carry out hydrogen bond repeated arch forming and bridge formation dissociation on a heat reversible target, and could reappear on him using hydrogen bond to this technical problem (JP,11-209524,A). This elastomer constituent can fully show a melting fluidity with the molding temperature of thermoplastics, such as olefin system resin which has not received denaturation, it has mechanical strengths, such as breaking strength which was excellent in low temperature with arch forming, and further research is advanced as a recyclable ingredient.

[0004]

[Problem(s) to be Solved by the Invention] In ordinary temperature, this invention forms the stable structure of cross linkage, has rubber elasticity, and aims at offering the thermoplastic elastomer which repeats hardening and fluidization by the temperature change and can be reproduced while it fully shows a melting fluidity with the molding temperature of usual thermoplastics.

[0005]

[Means for Solving the Problem] When this invention persons inquired wholeheartedly in order to get the ingredient which was excellent with the recycle nature to which arch forming and bridge formation dissociation are repeated by the temperature change, and physical properties do not fall as a line, they completed a header and this invention for between the molecules by the pi electron which a ring has, or an intramolecular interaction having been more excellent in the recycle nature of thermoplastic elastomer. That is, this invention offers the ring in which the substituent constant sigma of Hammett's rule has the substituent of a forward value, the ring in which said sigma has the substituent of a negative value, and the thermoplastic elastomer to which said sigma has at least two sorts chosen from non-permuted the ring and nitrogen-containing heterocycle of 0 in a side chain. In said thermoplastic elastomer, it is desirable to have at least two sorts chosen from the ring in which said sigma has the substituent of a forward value, the ring in which said sigma has the substituent of a negative value, and nitrogen-containing heterocycle in a side chain. It is desirable that the substituent of a forward value is at least one sort as which said sigma is chosen from a halogen radical, a phenyl group, a cyano group, a nitro group, an acetyl group, and a carboxyl group here. Moreover, it is desirable that the substituent of a negative value is at least one sort as

which said sigma is chosen from an alkyl group, a methoxy group, a phenoxy group, a hydroxyl group, and the amino group.

[0006] It is desirable that said thermoplastic elastomer has the ring in which said sigma has the substituent of a forward value, and the ring in which said sigma has the substituent of a negative value in a side chain. Or it is desirable that said thermoplastic elastomer has the ring in which said sigma has the substituent of a forward value, and nitrogen-containing heterocycle in a side chain. As for said thermoplastic elastomer, it is desirable to have a carbonyl content radical in a side chain further. Or said thermoplastic elastomer does not need to have a carbonyl content radical in a side chain. Furthermore, this invention offers the rubber constituent containing said thermoplastic elastomer.

[0007]

[Embodiment of the Invention] Below, this invention is explained in more detail. The thermoplastic elastomer of this invention is characterized by the ring in which the substituent constant sigma of Hammett's rule has the substituent of a forward value, the ring in which said sigma has the substituent of a negative value, and said sigma having at least two sorts chosen from non-permuted the ring and nitrogen-containing heterocycle of 0 in a side chain. It is desirable that they are at least two sorts as which said side chain is chosen from the ring in which said sigma has the substituent of a forward value, the ring in which said sigma has the substituent of a negative value, and nitrogen-containing heterocycle especially. Hammett's rule is a rule of thumb advocated by L.P.Hammett in 1935 here, in order to discuss quantitatively the effect of the substituent exerted on the reaction or balance of an organic compound. A substituent constant sigma is a constant decided by the class and location of a substituent, and it is known that there is an inclination which is set to sigma=0 in the case of not permuting and is set to sigma>0 with sigma<0 and an electronic suction nature machine in an electron releasing group.

[0008] As a ring which is not permuted [ whose sigma used for this invention is 0 ], the benzene ring is mentioned preferably, for example. Moreover, it is desirable that it is at least one sort as which halogen radicals, such as a fluorine atom and a chlorine atom, a phenyl group, a cyano group, a nitro group, an acetyl group, a carboxyl group, etc. are preferably mentioned, and are chosen from the inside of these as a substituent in which sigma used for this invention has a forward value. By having these substituents, there is an inclination for the pi electron consistency of a ring to increase. Especially a permutation location is not limited. When it has two substituents, any of alt.\*<sup>\*\*</sup> meta and Para are sufficient as this two substituent, and at least three or more pieces have it. [ same ]

[0009] It is desirable that sigma is at least one sort as which an alkyl group, a methoxy group, a phenoxy group, a hydroxyl group, the amino group, etc. are preferably mentioned, and are chosen from the inside of these as a substituent of a negative value. Especially a permutation location is not limited like the case where sigma is forward. As an alkyl group, the straight chain or branched chain of carbon numbers 1-20 is desirable, and it is more desirable that it is the straight chain or branched chain of carbon numbers 1-6. Specifically, a methyl group, an ethyl group, a propyl group, an isopropyl group, butyl, an isobutyl radical, t-butyl, n-hexyl group, etc. are mentioned preferably. The amino group may be an amino group which has substituents, such as a methyl group of 1 or 2, an ethyl group, and a propyl group, and, specifically, N and N-dimethylamino radical, N, and N-diethylamino radical etc. is preferably mentioned as an amino group

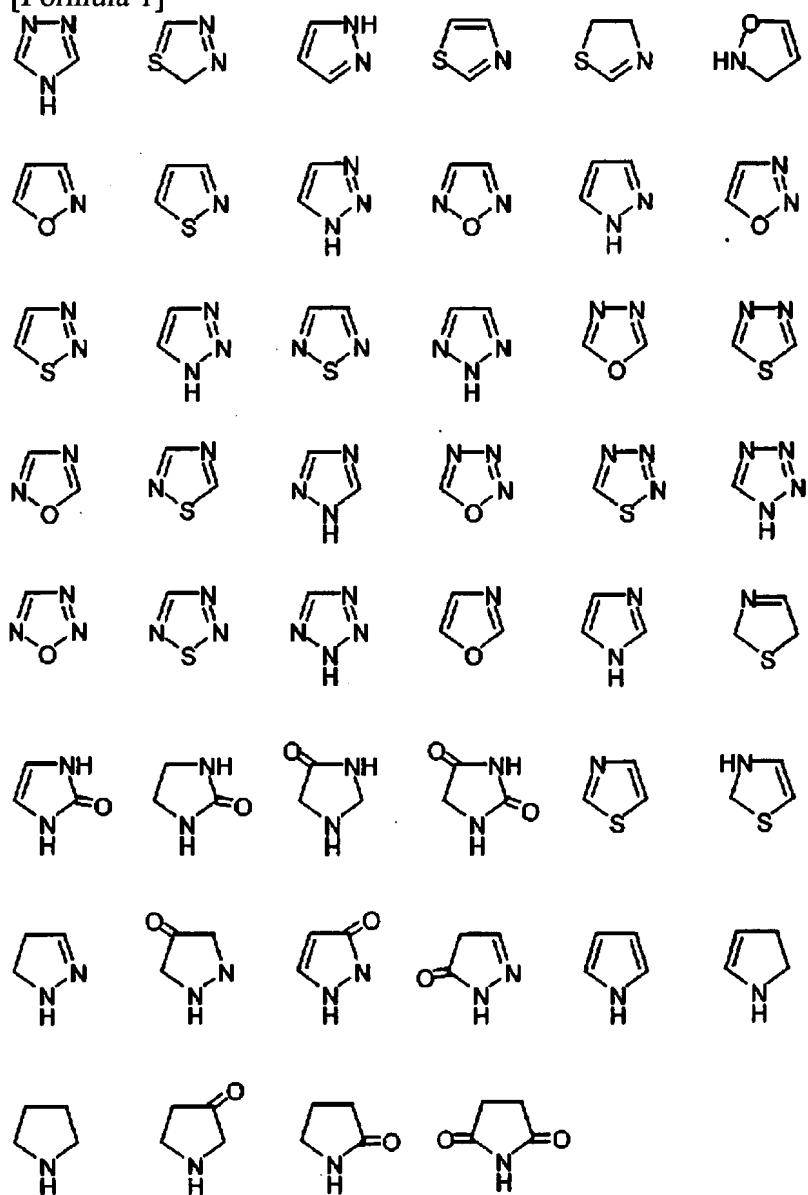
which has a substituent.

[0010] The thermoplastic elastomer of this invention may have the above-mentioned ring which the substituent of a non-permuted ring ( $\sigma=0$ ),  $\sigma>0$ , or  $\sigma<0$  combined in the side chain. Moreover, the thermoplastic elastomer of this invention may have nitrogen-containing heterocycle in the side chain.

[0011] Although it will not be limited as nitrogen-containing heterocycle used for this invention especially if a nitrogen atom is included as a ring member element, the oxygen atom, the sulfur atom, the Lynn atom, etc. may be included as a ring member element. For example, the five-membered ring type nitrogen-containing heterocycle shown below, triazine, thoria ZORIJIN, a pyridine, a pyrimidine, pyrazine, a quinoline, phenazine, a pteridine, etc. are used preferably.

[0012]

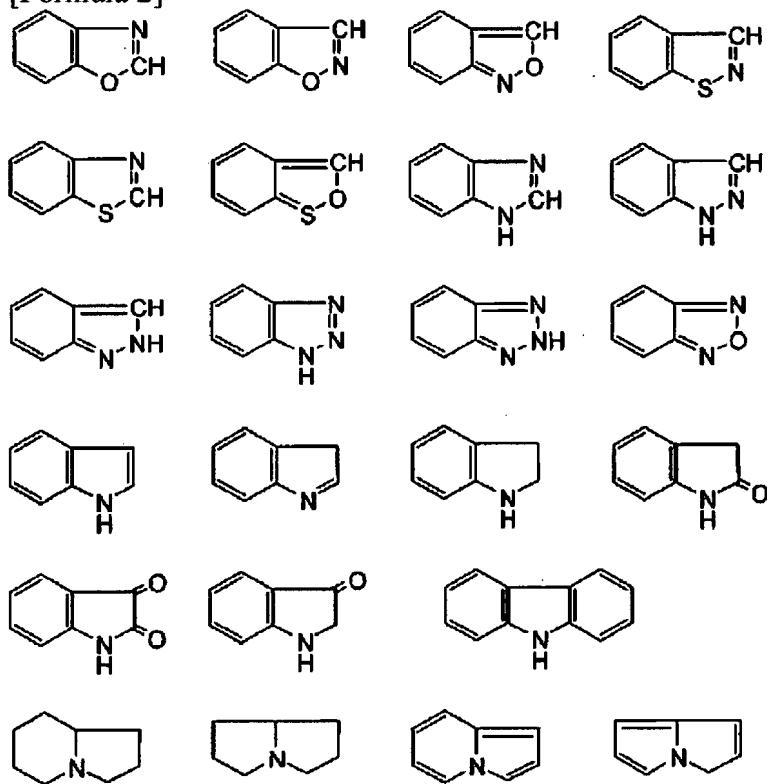
[Formula 1]



[0013] Moreover, what the benzene ring condensed, and the thing which the above-mentioned monocycle heterocycles condensed can also be used for the above-mentioned heterocycle, for example, the following condensed ring is mentioned preferably.

[0014]

[Formula 2]



[0015] You may have the substituent, halogen radicals, such as alkoxy groups, such as alkyl groups, such as a methyl group, an ethyl group, a propyl group (ISO), and a hexyl group, a methoxy group, an ethoxy radical, and a propoxy group (ISO), a fluorine, chlorine, and iodine, a cyano group, the amino group, an aromatic hydrocarbon radical, carboxyloxy group, a ether group, an acyl group, a thioether radical, etc. may be mentioned as a substituent, and the above-mentioned nitrogen-containing heterocycles may be such combination. Especially a permutation location is not limited and the number of substituents is not limited, either. Moreover, although it is not necessary to have it even if the above-mentioned heterocycle has aromaticity, since a strong interaction can be discovered more if it has aromaticity, it is desirable, and especially five-membered ring type nitrogen-containing heterocycle is excellent in this point especially. the above-mentioned heterocycle -- hydrogenation -- or you may \*\*\*\*.

[0016] The ring which has the above-mentioned substituent ( $\sigma > 0$  or  $\sigma < 0$ ), a non-permuted ring ( $\sigma = 0$ ), or nitrogen-containing heterocycle (henceforth [ these are named generically and ] "the ring structure of this invention") is introduced as a side chain of the elastomeric polymer which constitutes the principal chain of the thermoplastic elastomer of this invention.

[0017] Here, the elastomeric polymer used for this invention is explained. In this invention, as for an elastomeric polymer, glass transition temperature ( $T_g$ ) says the thing

of the polymer below a room temperature (25 degrees C). Generally the elastomeric polymer of this invention is naturally-occurring polymers well-known as a rubber elasticity ingredient for vulcanization (bridge formation, hardening), or synthetic macromolecule. As such an elastomeric polymer, olefin system rubber, such as diene system rubber, such as natural rubber, polyisoprene rubber, butadiene rubber, 1, 2-butadiene rubber, a styrene butadiene rubber, nitrile rubber, and chloroprene rubber, isobutylene isoprene rubber, ethylene-propylene system rubber (EPDM, EPM), chlorosulfonated polyethylene, acrylic rubber, and a fluororubber, epichlorohydrin rubber, polysulfide rubber, silicone rubber, polyurethane rubber, etc. are mentioned, for example. Moreover, you may be the thermoplastic elastomer (TPE) containing a resinous principle, for example, may be the polystyrene system TPE (SBS, SIS, SEBS) by which hydrogenation may be carried out, the polyolefine system TPE, the polyvinyl chloride system TPE, the polyurethane system TPE, the polyester system TPE, or the polyamide system TPE.

[0018] The above-mentioned elastomeric polymers may be any of the shape of liquefied or a solid-state. Moreover, although especially the molecular weight is not limited but it can choose suitably according to the purpose of use, crosslinking density, etc., liquid rubber is desirable when it gives priority to the convenience at the time of manufacturing thermoplastic elastomer, and the fluidity at the time of heating (debridge formation).

Moreover, it is desirable that it is molecular weight as shows the shape of liquid, for example, with diene system rubber, such as polyisoprene rubber and butadiene rubber, 1, and 000-100,000 have desirable weight average molecular weight, and it is more desirable that it is 10 and 000 to about 100,000. On the other hand, when it gives priority to the reinforcement of rubber, solid-state rubber is desirable, 100,000-2,000,000 have desirable weight average molecular weight, and 300,000-1,000,000 are more desirable.

[0019] If the thermoplastic elastomer of this invention repeats arch forming and bridge formation dissociation on a heat reversible target by having the ring structure of this invention in the above-mentioned elastomeric polymer at a side chain, can reappear, it has rubber elasticity below 120 degrees C, tensile strength is very high and it exceeds 120 degrees C, a fluidity will be given and a remolding will become possible, and moreover, it becomes the ingredient which physical properties did not fall even if carried out by repeating arch forming and bridge formation dissociation, but was excellent in recycle nature. Moreover, by the case of the elastomeric polymer for which a bridge is not constructed before introducing a side chain, even if it fabricates by carrying out cold flow, it is difficult to hold the original form, but once it fabricates, unless it reheats according to false bridge formation, it excels in the point that a configuration is held at the thermoplastic elastomer of this invention at a moldability. It is considered by such effectiveness for the interaction of the pi electrons on a ring to have contributed. That is, although the electric interaction of pi electrons is formed between molecules or by intramolecular and false bridge formation is formed at \*\*\*\*\* and below a certain temperature, if the temperature currently heated is exceeded, molecular motion will become active, it will become impossible to hold bridge formation consequently, and it will be thought that it is tintured with a fluidity. Moreover, the thermoplastic elastomer of this invention has high flexibility compared with the case where false bridge formation is introduced into thermoplastics. Generally, reinforcement is taken out with the false bridge formation by the mutual attraction between a principal chain or a side chain,  $T_g$  of

thermoplastics is very high, it is deficient in it in flexibility, and it is very hard. The thermoplastic elastomer of this invention has low Tg to it, and attraction is for \*\*\*\*\* only to a bridge formation part.

[0020] As a side chain of this invention, although at least two sorts in an above-mentioned ring structure are included, it is desirable to have the ring to which the interaction between pi electrons is raised more and in which it combines, namely, sigma has the substituent of a forward value, and the ring in which sigma has the substituent of a negative value from an above-mentioned viewpoint. Or it is desirable to have the ring in which sigma has the substituent of a forward value, and nitrogen-containing heterocycle in a side chain. By combining these side chains, the interaction between pi electrons is for \*\*\*\*\* complementary at the intramolecular between molecules.

[0021] Although the ring structure of this invention may be coupled directly with the principal chain, it is desirable to have joined together from a viewpoint on composition through joint radicals, such as an amide group, a methylene group, ethylene, carbonyloxy group, and a thioether radical, by making the compound containing the radical which can carry out covalent bond to principal chains, such as these ring machines, the amino group and a hydroxyl group, a carboxyl group, a thiol group, or a sulfide radical, react. It is desirable at the point that especially an amide group and carbonyloxy group form complementary hydrogen bond also among these.

[0022] Moreover, in addition to the ring structure of above-mentioned this invention, the thermoplastic elastomer of this invention may have the carbonyl content radical further in the same side chain as a ring structure or another side chain of this invention. As for a carbonyl content radical, an amide, carbonyloxy, imide, a carboxyl group, etc. are mentioned. Especially the compound that can introduce such a radical is not limited, for example, a carboxylic-acid compound, its derivative, etc. are mentioned. As a carboxylic-acid compound, the organic acid which has the hydrocarbon group of saturation or partial saturation may be mentioned, and hydrocarbon groups may be any, such as aliphatic series, an alicycle group, and aromatic carboxylic acid. Moreover, as a carboxylic-acid derivative, a carboxylic anhydride, ester, a ketone, amino acid, amides, imide, a thiocarboxylic acid (sulphydryl group content carboxylic acid), etc. are mentioned.

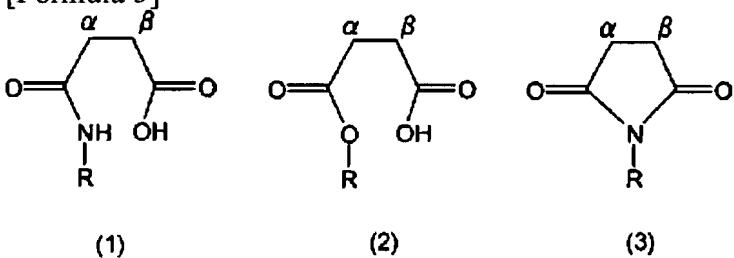
[0023] Specifically A malonic acid, a maleic acid, a SUKUSHIN acid, a glutaric acid, a phthalic acid, Isophthalic acid, a terephthalic acid, p-phenylenediacetic acid, para hydroxybenzoic acid, A carboxylic acid and substituent content carboxylic acids, such as p-aminobenzoic acid and mercaptoacetic acid, A succinic anhydride, a maleic anhydride, an anhydrous glutaric acid, phthalic anhydride, a propionic anhydride, Acid anhydrides, such as a benzoic anhydride, a maleate, malonic ester, Aliphatic series ester, such as SUKUSHIN acid ester, glutarate, and ethyl acetate, Phthalic ester, isophthalic acid ester, terephthalic-acid ester, Aromatic series ester, such as ethyl-m-amino benzoate and methyl-p-hydroxy benzoate, Ketones, such as a quinone, anthraquinone, and a naphthoquinone, a glycine, fricin, The vicine, an alanine, a valine, a leucine, a serine, threonine, a lysine, An aspartic acid, glutamic acid, a cysteine, a methionine, a proline, N -(p-amino benzoyl)- Amino acid, such as beta-alanine, a mallein amide, A mallein amic acid (mallein monoamide), the succinic-acid monoamide, 5-hydroxy valeric amide, Imide, such as amides, such as hydroxyethylacetamid, N, and N'-hexa methylenebis (acetamide), a chestnut amide, cycloserine, 4-acetamidophenol, and p-acetamide benzoic acid, maleimide, and a succinimide, is mentioned.

[0024] Also among these, it is desirable as a carbonyl content radical of this invention to be led from cyclic anhydrides, such as a succinic anhydride, a maleic anhydride, an anhydrous glutaric acid, and phthalic anhydride, and especially being led from a maleic anhydride is more desirable.

[0025] The ring structure of this invention combines the above-mentioned cyclic anhydride with an elastomeric polymer, it can make the compound which has the above-mentioned ring structure and a covalent-bond nature machine able to react, can carry out ring breakage of the cyclic anhydride, and can also be made to combine it with the same side chain. When it has in the same side chain, since the recycle nature of this invention is raised more, the side chain of this invention is desirable by having the structure shown in for example, the following type (1), (2), or (3).

〔0026〕

[Formula 3]



Here, R expresses the ring structure of this invention and combines with a principal chain at least by alpha or beta.

[0027] When the side chain of the thermoplastic elastomer of this invention has the structure of above-mentioned formula (1) - (3), in addition to the interaction between the above-mentioned pi electrons, between intramolecular or a molecule, a carbonyl group, a hydroxyl group or an imino group, a carboxyl group, an amide group, etc. can also form hydrogen bond, and it is thought that false bridge formation reinforcement is raised more. Furthermore, the interactions (NH-pi, OH-pi, CH-pi interaction, etc.) of these hydrogen bond nature machines and pi electrons may have contributed, and this invention person thinks that recycle nature of the thermoplastic elastomer of this invention was realized, as a result of contribution of the interaction of these plurality combining.

[0028] In this invention, it is desirable to have at a rate of 0.1 - 50 weight section to the principal chain partial 100 weight section, 0.1 - 35 weight section comes out comparatively, and a certain thing of the rate of a side-chain part (moiety) is more desirable. When for example, a principal chain part is polyisoprene rubber, the monomer of this rate into which per isoprene monomeric unit mol and a side-chain part were introduced is about 0.1-35 mol %. If it is this within the limits, the balance of the interaction of these side chains will be good at the intramolecular between molecules, and the tensile strength at the time of bridge formation of the thermoplastic elastomer of this invention will be very high, and it will become a thing with rubber elasticity. In under the 0.1 weight sections, since rubber elasticity will be spoiled if the reinforcement at the time of bridge formation is not enough and exceeds 50 weight sections, the rate of a side-chain part is not desirable. When it has a carbonyl content radical as an independent side chain, since the rate with the side chain which has the ring structure of this invention can discover a complementary interaction with it being 1:1, it is desirable. Moreover, as for the thermoplastic elastomer of this invention, it is desirable that the glass transition

temperature is 25 degrees C or less to obtain the rubber elasticity of a request in ordinary temperature.

[0029] Especially the manufacture approach of the thermoplastic elastomer of this invention is not limited, but can be compounded by the usual approach. For example, in having a carbonyl content radical and the above-mentioned ring structure in the same side chain, it usually obtains the compound which has an above-mentioned ring structure and an above-mentioned covalent-bond nature machine for the elastomeric polymer by which conversion was carried out by the carbonyl content radical from a room temperature by making it react for 3 to 5 hours at about 200 degrees C. The above-mentioned denaturation elastomeric polymer agitates diene system rubber, such as butadiene rubber, and the toluene solution containing mercaptoacetic acid under nitrogen-gas-atmosphere mind at a room temperature for 1 hour, settles a reaction mixture to a methanol, and is obtained by carrying out reduced pressure drying. Moreover, a commercial item can also be used, for example, they are LIR-403, -410, and -410A (above). Maleic-anhydride denaturation polyisoprene rubber, such as the Kuraray Co., Ltd. make, the KURAI nak 110, -221, -231 (above) Carboxyl denaturation polybutenes, such as carboxyl denaturation nitrile rubbers, such as the poly sir company make, CPIB (the Nippon Oil chemistry company make), and HRPPIB (Nippon Oil chemistry lab prototype), NYUKURERU (the Mitsui DEYUPON poly chemical company make), YUKARON (Mitsubishi Chemical make), etc. are mentioned. Moreover, after combining beforehand the compound which has a carbonyl content radical, and the above-mentioned ring structure and a covalent-bond nature machine, it can also be made to introduce into the side chain of an elastomeric polymer.

[0030] In not having a carbonyl content radical and the above-mentioned ring structure in the same side chain but introducing as a mutually-independent side chain The monomer which can form the principal chain of this polymer at the time of manufacture of an elastomeric polymer, Copolymerization of the copolymerization monomer which can introduce the above-mentioned radical is carried out, the above-mentioned thermoplastic elastomer may be manufactured directly, a principal chain (elastomeric polymer) may be beforehand formed by a polymerization etc., and, subsequently graft denaturation may be carried out with the compound which can introduce the above-mentioned radical.

[0031] In each manufacture approach, it can check whether each radical of the side chain of an elastomeric polymer is combined independently, or it joins together mutually with analysis means usually used, such as NMR and an IR spectrum.

[0032] The thermoplastic elastomer of this invention obtained as mentioned above can be mixed with carbon black, and can also be used as a constituent. Carbon black is suitably chosen according to an application. Generally, carbon black is classified into hard carbon and soft carbon based on particle diameter. The reinforcement nature of soft carbon to rubber is low, and the reinforcement nature of hard carbon to rubber is [ soft carbon ] strong, using the strong hard carbon of reinforcement nature especially in this invention -- desirable -- the thermoplastic-elastomer 100 weight section -- receiving -- 10 - 70 weight section -- it is preferably good 20 - 60 weight section and to be by 30 - 50 weight \*\*\*\*\* more preferably.

[0033] Moreover, other reinforcing agents, such as a silica, an antioxidant, an antioxidant, a pigment, etc. can also be added in the range which does not spoil the purpose of this invention. As other reinforcing agents, fumed silica, a baking silica, a

sedimentation silica, a grinding silica, fused silica, a silicious marl, ferrous oxide, a zinc oxide, titanium oxide, the barium oxide, a magnesium oxide, a calcium carbonate, a magnesium carbonate, zinc carbonate, agalmatolite clay, kaolin clay, baking clay, etc. are mentioned, and it is good 20 - 80 weight section and to carry out 30-60 weight section addition more preferably to the thermoplastic-elastomer 100 weight section. As an antioxidant, for example, compounds, such as a hindered amine system of a hindered phenol system, aliphatic series, and aromatic series, are mentioned, and it is good 0.1 - 10 weight section and to carry out 1-5 weight section addition more preferably to the thermoplastic-elastomer 100 weight section. as an anti-oxidant -- butylhydroxytoluene (BHT) and burylhydroxyanisole (BHA) etc. -- it is mentioned and it is good 0.1 - 10 weight section and to carry out 1-5 weight section addition more preferably to the thermoplastic-elastomer 100 weight section. As a pigment, organic pigments, such as inorganic pigments, such as a titanium dioxide, a zinc oxide, ultramarine blue, red ochre, a lithopone, lead, cadmium, iron, cobalt, aluminum, a hydrochloride, and a sulfate, an azo pigment, and a copper-phthalocyanine pigment, etc. are mentioned, and it is good 0.1 - 10 weight section and to carry out 1-5 weight section addition more preferably to the thermoplastic-elastomer 100 weight section.

[0034] Although self-bridge formation of the thermoplastic elastomer of this invention can be carried out, it is the range which does not spoil the purpose of this invention, and can also use together a vulcanizing agent, a vulcanization assistant, a vulcanization accelerator, etc. As a vulcanizing agent, sulfur system vulcanizing agents, such as powder sulfur, sedimentation nature sulfur, high dispersibility sulfur, surface-preparation sulfur, insoluble sulfur, JIMORUFO phosphorus disulfide, and alkylphenol disulfide, a zinc white, magnesium oxide, a litharge, p-quinonedioxime, p-dibenzoyl quinonedioxime, tetra-chloro-para benzoquinone, Polly p-dinitroso benzene, MECHIRIN dianiline, etc. are mentioned. As a vulcanization assistant, fatty-acid zinc, such as fatty-acid; acetyl acid zinc, such as an acetyl acid, a propionic acid, butanoic acid, stearic acid, an acrylic acid, and a maleic acid, zinc propionate, butanoic acid zinc, zinc stearate, acrylic-acid zinc, and maleic-acid zinc, etc. is mentioned. Thiazole systems [, such as a thiuram system; hexamethylenetetramine /, such as guanidine system:dibenzothiazyl disulfide (DM), such as aldehyde ammonia system; diphenylguanidine ], such as a vulcanization accelerator, and tetramethylthiuramdisulfide (TMTD), a tetraethylthiuram disulfide (TETD); sulfenamide system [, such as cyclohexylbenzothiazyl sulfene AMAIDO, ]; etc. is mentioned. Furthermore, alkylphenol resin, its halogenide, etc. can also be used.

[0035] The thermoplastic-elastomer constituent of this invention can utilize rubber elasticity, and can use it for various vulcanized-rubber applications. Moreover, if it is made to contain in hot melt adhesive, thermal resistance and recycle nature can be raised. Especially The circumference of an automobile, for example, the tread of a tire, the radiator grille of carcass; sheathing, a side mall, a garnish (a pillar, rear \*\* cowl top), and aero parts (an air dam --) SUPORIRA, a wheel cover, a weather strip, an air outlet louver, an air scoop, a hood blister, a ventilation regio-oralis article, and corrosive protection cure components (an exaggerated fender --) A side seal panel, a mall, a window, a hood, a door belt, Marks; A door, a light, the weather strip of a wiper, a glass run, Components for interior window frames, such as a glass run channel; An air duct hose, a radiator hose, Brake hose; A crankshaft seal, bulb oil flinger, a cylinder-head-cover gasket, An A/T oil-cooler hose, missions oil seal, a P/S hose, Lubricating oil system components, such as P/S

oil seal; A fuel hose, an emission control hose, Fuel system components, such as an inlet filler hose and tire FURAMU; An engine mount, Components for vibrationproofing, such as in tank pump mounting; Boots; A/C hose, such as a CVJ boot and a rack & pinion boot, Components for air-conditioning, such as an A/C seal; it can use suitable for belt components; window shielding sealer [, such as a timing belt and a belt for auxiliary machinery, ], vinyl plastisol sealer, anaerobic sealer, body sealer, and spot weld sealer; etc. Moreover, if it is made to contain in the resin or rubber which starts cold flow at a room temperature as for example, a flow inhibitor as a modifier of rubber, the flow and cold flow at the time of extrusion can be prevented. Moreover, tensile strength, tear strength, and flexural strength can be further raised by including carbon black etc.

[0036]

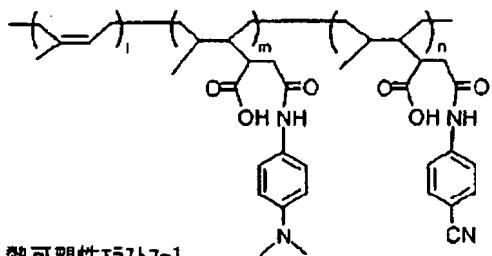
[Example] Although an example is given to below and this invention is more concretely explained to it, this invention is not limited to these examples. First, physical properties were evaluated about thermoplastic-elastomer A which has the ring in which sigma has the substituent of a forward value, and the ring in which sigma has the substituent of a negative value in a side chain.

0.599g (Tokyo formation shrine make) (4.4mmol) of N and N-dimethyl-p-phenylene diamines was added to maleic-anhydride denaturation polyisoprene-rubber (rate % and LIR of denaturation-410A, Kuraray Co., Ltd. make) 17.10g (8.8mmol) of <composition of thermoplastic elastomer 1> marketing, and heating churning was carried out at 130 degrees C for 3 hours. [ of 2.7 mols ] Subsequently, 4-amino benzonitrile (Tokyo formation shrine make) 0.52g (4.4mmol) was added to this reactant, and heating churning was carried out at 130 degrees C for 3 hours. After checking having become homogeneity, the gel reactant was obtained by leaving it overnight. The reactant checked that it was the thermoplastic elastomer 1 which has the following typical structure by NMR and IR.

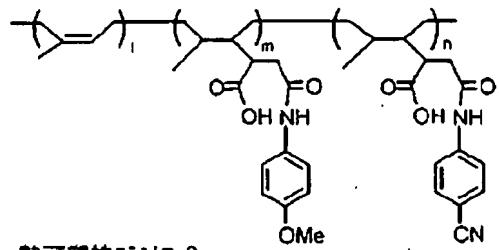
[0037] The corresponding compound was hereafter used at same rate similarly, and thermoplastic elastomer 2-5 was compounded. Moreover, as a comparison compound, 1.09g (8.01mmol) of above-mentioned maleic-anhydride denaturation polyisoprene-rubber 15.56g (8.01mmol), N, and N-dimethyl-p-phenylene diamines was made to react, and thermoplastic elastomer 6 was obtained. Moreover, it replaced with N and N-dimethyl-p-phenylene diamine, and if it removed having used 4-amino benzonitrile at same rate, thermoplastic elastomer 7 was obtained like thermoplastic elastomer 6. Furthermore, it replaced with N and N-dimethyl-p-phenylene diamine, and if it removed having used p-amino acetophenone at same rate, thermoplastic elastomer 8 was obtained like thermoplastic elastomer 6. The typical structure of the obtained thermoplastic elastomer 1-8 is as follows.

[0038]

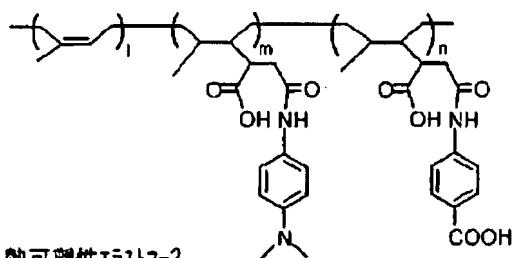
[Formula 4]



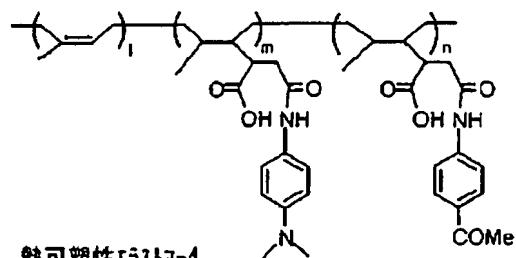
熱可塑性エラストマー-1



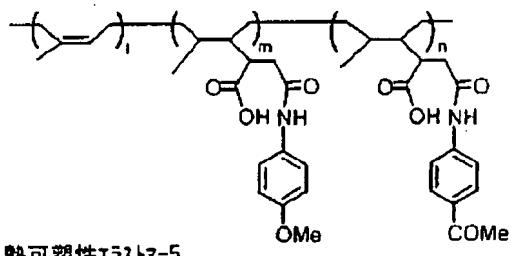
熱可塑性エラストマー-2



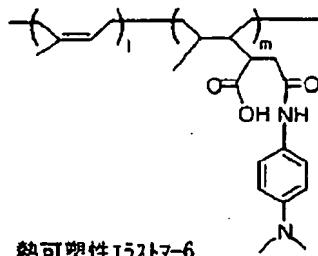
熱可塑性エラストマー-3



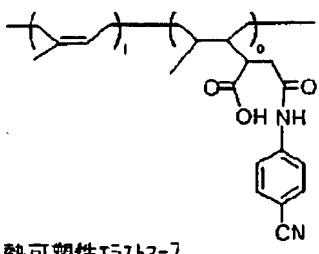
熱可塑性エラストマー-4



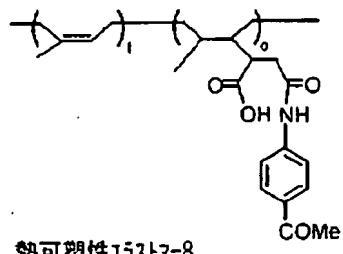
熱可塑性エラストマー-5



熱可塑性エラストマー-6



熱可塑性エラストマー-7



熱可塑性エラストマー-8

Here, it is 1:m:n\*\*97.3:1.35:1.35 and 1:o\*\*97.3:2.7.

[0039] About the thermoplastic elastomer 1-5 obtained example 1-5, it is JIS. A degree of hardness was measured and the condition at the time of 120-degree-C heating was observed. In addition, JIS The measuring method of A degree of hardness is as below-mentioned.

[0040] It is JIS like [ thermoplastic elastomer / 6-8 / which was obtained example of comparison 1-3 ] examples 1-5. A degree of hardness and the condition at the time of 120-degree-C heating were observed. A result is shown in the 1st table.

[0041] (JIS A degree of hardness) After carrying out press forming of the obtained

thermoplastic elastomer 1-5 for 60 minutes at 150 degrees C, the 5cm 1cm[ in thickness ] x long and 5cm wide monotonous sample was produced. They are a three-sheet pile and JIS about the obtained monotonous sample. It is based on K6253 and is JIS at a room temperature. A degree of hardness was measured.

[0042]

[Table 1]

第 1 表

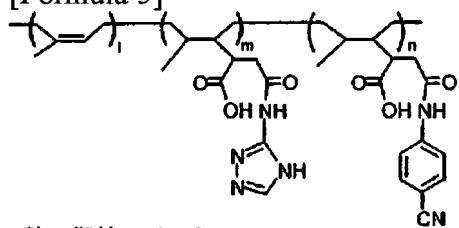
	実 施 例					比 較 例		
	1	2	3	4	5	1	2	3
熱可塑性ゴム	1	2	3	4	5	6	7	8
JIS A 硬度	15	13	12	10	13	液状	液状	液状
120 ℃加熱時の状態	液状	液状	液状	液状	液状	液状	液状	液状

[0043] Next, sigma evaluated physical properties about thermoplastic-elastomer B which has the ring which has a forward substituent, and nitrogen-containing heterocycle in a side chain.

0.766g (Tokyo formation ABA, shrine make) (5.585mmol) of 4-aminobenzoic acids was added to maleic-anhydride denaturation polyisoprene-rubber (rate % and LIR of denaturation-410A, Kuraray Co., Ltd. make) 16.2857g (8.382mmol) of <composition of thermoplastic elastomer 9> marketing, and heating churning was carried out at 130 degrees C for 2 hours. [ of 2.7 mols ] After checking having become homogeneity, the gel reactant was obtained by leaving it overnight. Subsequently, 3-amino-1,2,4-triazole (ATA, Japanese carbide company make) 0.2349g (2.79mmol) was added to this reactant, and heating churning was carried out at 160 degrees C for 3 hours. After checking having become homogeneity, the gel reactant was obtained by leaving it overnight. The reactant checked that it was the thermoplastic elastomer 9 which has the following typical structure by NMR and IR.

[0044]

[Formula 5]



熱可塑性ゴム-9

It is here and is l:m:n\*\*97.3:1.35:1.35[0045]. Hereafter, similarly, the mixing ratio of 4-aminobenzoic acid, 3-amino-1,2,4-triazole, 4-aminopyridine (Tokyo formation 4AP, shrine make), and 3-aminopyridine (Tokyo formation 3AP, shrine make) was changed, and thermoplastic elastomer 10-15 was compounded. In addition, the value of  $(m+n)/(l+m+n)$  in thermoplastic elastomer 9 is the same also about thermoplastic

elastomer 10-15. The mixed mole ratio of each nine to thermoplastic-elastomer 15 raw material is shown in the 2nd table. Moreover, as a comparison compound, the above-mentioned maleic-anhydride denaturation polyisoprene-rubber 16.28g (8.379mmol) and 1.149g (8.379mmol) of 4-aminobenzoic acids were made to react, and thermoplastic elastomer 16 was obtained. Furthermore, it replaced with 4-aminobenzoic acid, 4-aminopyridine was used at same rate, and thermoplastic elastomer 17 was obtained like thermoplastic elastomer 16.

[0046] About the thermoplastic elastomer 9-15 obtained example 6-12, it is JIS at a room temperature. A degree of hardness was measured and the condition at the time of 120-degree-C heating was observed. JIS The measuring method of A degree of hardness is as above-mentioned.

[0047] It is JIS like [ thermoplastic elastomer / the example 4 of a comparison, and / 16 and 17 / which was obtained five ] examples 6-12. A degree of hardness and the condition at the time of 120-degree-C heating were observed. A result is shown in the 2nd table.

[0048]

[Table 2]

第 2 表

	実 施 例							比 較 例	
	6	7	8	9	10	11	12	4	5
熱可塑性エラストマー	9	10	11	12	13	14	15	16	17
ATA (モル)	3/1	1/2	2/3	0	0	0	0	0	0
4AP (モル)	0	0	0	1/3	1/2	2/3	0	0	1
ABA (モル)	2/3	1/2	1/3	2/3	1/2	1/3	1/2	1	0
3AP (モル)	0	0	0	0	0	0	1/2	0	0
JIS A 硬度	36	38	43	31	32	32	11	液状	液状
120 °C 加熱時の状態	液状	液状	液状	液状	液状	液状	液状	液状	液状

[0049]

[Effect of the Invention] If this invention is followed as explained in full detail above, even if it repeats arch forming and bridge formation dissociation by the temperature change to an elastomeric polymer and reappears to it by introducing a carbonyl content radical into a side chain the ring structure of this invention, and if needed, physical properties, such as rubber elasticity, will not fall but the thermoplastic elastomer which was excellent at recycle nature will be obtained. Desired tensile strength is obtained by choosing the combination of the ring structure of this invention according to an

application.

---

[Translation done.]